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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003905088 for a patent by CIBA SPECIALTY CHEMICALS PTY LTD as filed on 17 September 2003.

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PROVISIONAL SPECIFICATION

Invention Title: POLYMERIC COMPOSITIONS

Applicant: CIBA SPECIALTY CHEMICALS PTY LTD

The invention is described in the following statement:

POLYMERIC COMPOSITIONS

The present invention relates to improved polymeric compositions having laser-marking properties.

BACKGROUND

The marking of, and printing onto, polymeric materials in an indelible fashion is required in many different applications. Domestic articles, engine parts for automobiles, key tops for computer keyboards and other similar products are often marked with letters, symbols or other markings. Such markings can be applied by using a curable ink. However, there are usually high production costs involving using such inks as the application and curing of the inks involves a number of separate steps.

An alternative is laser marking. In laser marking a laser is used in conjunction with a polymeric material which has incorporated therein a chemical. The wavelength of the laser beam is synchronized with the chemical to cause the polymeric material to burn resulting in a clear contrast between the irradiated area and the rest of the product.

For example, EP0867466 teaches a polyolefin resin composition comprising 100 parts by weight of a polyolefin resin and 0.01 to 20 parts by weight of a black pigment mainly comprising a metal oxide. When a laser beam is applied to the resin, the black pigment decomposes in the irradiated areas and is completely released. As a result lighter coloured markings are obtained in contrast to the unmarked area of the moulded article, which is black.

However, in many circumstances it is desirable to mark a polymeric product which is brightly coloured. The polyester resin composition of EP08674666 is capable of only providing white barcode markings against a black background and therefore is not useful if the background area is a lighter colour.

JP 2001071645 describes a resin composition comprising a thermoplastic resin, a sulphide and pigments including coloured pigments and a black stain pigment – in particular carbon black having a mean particle size of 10 to 90nm. When a laser beam at a wavelength of 354nm to 1064nm is applied to the resin, the carbon black absorbs the laser beam, converts it into heat energy and a marking with a "very high degree of black" is obtained. This black barcode is said to contrast with the non-irradiated area of the moulded article. However, it has been found that this particular resin composition does not work well where the background is a colour such as pink or yellow.

One particular area where coloured resins are used is for the production of livestock items such as ear tags. Ear tags are traditionally used by farmers as a means of tracking and readily identifying stock. Tags are typically made of thermoplastic resins and are marked with letters, patterns, barcodes or symbols. In the context of handling livestock it is desirable to use different coloured thermoplastic resins preferably bright colours such as yellow and pink to enable handlers to readily segregate and group livestock. There is a need in this application, and of course many other applications, where the laser marking of brightly coloured polymeric compositions is desirable. Accordingly, it is an object of the present invention to provide an improved polymeric composition which enables a laser marking process to be used to produce a dark marking particularly where the polymeric composition is brightly coloured.

SUMMARY OF INVENTION

In one aspect of the present invention there is provided a polymeric composition having laser-marking properties said polymeric composition including a polymeric material, mica or a micaceous material and a metallic sulphide.

Surprisingly it has been found that when a laser beam is applied to the surface of an article formed from such a polymeric composition prominent and good black marking is achieved in the irradiated areas. It is believed by the applicant that the mica or micaceous material absorbs the laser radiation, which creates a localised heat. This is believed to cause the sublimation of the metallic sulphide

in the irradiated area and as the metallic sulphide vaporises the surface of the polymeric composition becomes charred. The resulting marks are dark and are visible against the non-irradiated background.

In a second aspect of the present invention there is provided a moulded article; said article being moulded from a polymeric composition which includes a polymeric material, mica or a micaceous material, and a metallic sulphide; wherein such moulded article is adapted to exhibit dark markings in areas irradiated with a laser beam.

In a third aspect of the present invention there is provided a method of producing a moulded article having laser marked surface portions, said method including:

(a) providing a polymeric material;

(b) compounding said polymeric material with mica or a micaceous material and a metallic sulphide to provide a polymeric composition;

(c) moulding an article using the polymeric composition; and

(d) irradiating said article with a laser beam to produce laser marked surface portions on the article.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term "marking" refers to any laser mark whatsoever and is not limited to letters. It includes the application of patterns, barcodes, symbols or drawings and the like.

The polymeric material used in the present invention is not particularly limited and may include a wide range of thermoplastic resins selected from the group consisting of polyolefins, polyurethanes, polycarbonates, polyolefins, polycarbonates, polyesters, rubber modified monovinylidene, aromatic resins, polyetherimides, polyamides, polyester carbonates, polyphenylene sulphides, polyamideimides, polyesteramides, polyether esters, polyetherimide esters, polyarylates, polymethylpentenes, polysulfones, polyethersulfones, polystyrenes, rubber modified high impact polystyrenes, acetyles, styrene

maleic anhydride copolymers, acrylonitrile styrene acrylate copolymers, polyphenylene ethers, polyether ketones, chlorinated polymers, fluorinated polymers, and liquid crystal polymers. In a more preferred aspect the thermoplastic resins are selected from the group consisting of polyurethanes, polycarbonates and rubber modified monovinylidene aromatic resins and blends thereof. In an even more preferred aspect the thermoplastic resin is a polyurethane resin.

Given the desire for a lighter coloured product or article, polyesters, polyurethanes, polycarbonates and rubber modified monovinylidene aromatic resins and blends thereof are particularly well suited for laser marking according to the present invention. In a more preferred aspect a polyurethane resin is employed.

Additional pigments, dyes and/or inert fillers may be added to the polymeric composition of the invention depending on the desired background colour. The kinds and amounts of these additives are decided appropriately in accordance with the end use. In particularly preferred compositions pigments are used so that a product moulded using the composition would be pink, red, yellow, orange, lime green, lilac, mid to light blue or turquoise in colour.

Mica is a complex potassium aluminium silicate and may also have a synthetically treated surface or doped structure containing metal oxides, e.g. such as oxides of antimony and/or titanium and/or tin, etc with a density of 2.8 to 4.0 g/cm^3, a Mohs hardness of 2.5. to 4 and oil absorption values of 35 to 70.0 grams per 100 grams of powder. Preferably the mica or micaceous material is present in an amount sufficient to absorb the intended level of laser radiation. Preferably the amount of mica ranges from 0.05 to 1 percent by weight based on the total weight of the composition. Even more preferably the amount of mica present is about 0.3 percent by weight based on the total weight of the composition.

The metallic sulphide is preferably selected from the group consisting of copper sulphide; cadmium sulphide, iron sulphide, cobalt sulphide, zinc sulphide or nickel sulphide. Most preferably the metallic sulphide is zinc sulphide.

The amount of the metallic sulphide present in the polymeric composition is preferably sufficient to produce a dark marking on the moulded article when it has been irradiated with a laser beam at an irradiation level of 5-50 ampere at a frequency of 1-100kHz in the range of 500-2100nm. More preferably the amount of metallic sulphide present in the polymeric composition ranges from 0.3 to 3 percent by weight based on the total weight of the composition. Even more preferably the metallic sulphide is zinc sulphide and is present in an amount of about 1.7 percent by weight based on the total weight of the composition.

Further additives may be incorporated into resin composition to improve the moulding properties of the resin or environmental adaptability of the resulting moulded articles. Useful additives include antioxidants, antistatic agents, light stabilizers, UV absorbers, neutralizing agents, rust inhibitors, lubricants, flame retardants, nucleating agents, dispersants, processing stabilizers, flow improvers, and the like. The kinds and amounts of these additives are decided appropriately in accordance with the end use.

The polymeric composition of the present invention may be prepared by compounding the above-described polymeric material, metallic sulphide and mica and, if desired, further additives. The compounding method is not limited, and any known technique can be adopted. Preferably the method is carried out either by intensive shear z blade mixing or by extrusion (single screw or twin screw counter or co-rotating).

The method for moulding the polymeric composition is not particularly restricted. For example, extrusion, press moulding, injection moulding, blow moulding, and the like can be used to mould the composition. The effects of the present invention are noticeably manifested particularly when the polymeric composition

is injection moulded because the resulting injection moulded articles are excellent in surface appearance such as gloss and uniformity.

The resulting moulded article can readily marked with letters, patterns, barcodes, symbols, drawings etc. by scanning with a laser beam. Lasers used for marking are not limited and include gas lasers, such as a carbon dioxide laser, an excimer laser, and an argon laser, and solid lasers, such as a ruby laser, a semiconductor laser, and a YAG laser. One preferred laser used is a Nd:YAG laser operating at a wavelength of 1064nm; having a pulse frequency of 6200Hz; a scanning speed of 1600 mm/sec and a laser power of 26.5 amps.

It should be noted that because the polymeric material itself shows little absorption at the wavelength of laser irradiation, the laser marking does not affect the practical performance of the moulded article.

The present invention will now be illustrated in greater detail with reference to an Example, but it should be understood that the present invention is not construed as being limited thereto. Unless otherwise noted, all the percents are by weight.

EXAMPLE A

PA1997 UV	5.00%
CAS No 112945-52-5	0.13%
CAS No. 13463-67-7	2.02%
CAS No. 154946-66-4	0.195%
CAS No. 5590-18-1	0.096%
Mecon MP 105	0.075%
Iriodin LS825	0.3%
CAS No. 1314-98-3	1.7%
Elastollan WY01388	90.484%

In the abovementioned description in each case where a "CAS" number is recited it is the Chemical Abstracts Service registry number. PA 1997 UV consists of the following:-

CAS No. 6683-19-8	3.00%
CAS No. 2440-22-4	10.00%
CAS No. 65447-77-0	10.00%
CAS No. 112945-52-5	1.50%

CAS No. 471-34-1 30.16%
Elastollan WY01388 45.50%

Mecon MP 105 is a product of Sadolin, Iriodin LS825 is a product of Merck, Inc. and Elastollan WY01388 is a product of BASF.

These materials were compounded in a z blade mixer at 190°C for approximately 20 seconds after flux. The sample was then compression moulded at 200°C for 2-3 minutes at 200psi and then cooled.

Subsequent plaque was then mounted and laser marked using an Nd:YAG laser operating at a wavelength of 1064 nm.

The laser marked moulded articles of the invention may be used for any application in which it is necessary for such indicia to be visible. By way of example it is contemplated that the polymeric compositions could be compounded to form a livestock product such as an ear tag and subsequently marked using laser processing to enable livestock handlers to track and readily identify stock.

While the invention has been described in detail and with reference to specific examples thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

The claims defining the invention are as follows:

1. A polymeric composition having laser marking properties which includes a polymeric material, mica or a micaceous material and a metallic sulphide.

2. A polymeric composition according to claim 1, wherein the polymeric material is a thermoplastic resins selected from the group consisting of polyolefins, polyurethanes, polycarbonates, polyolefins, polycarbonates, polyesters, rubber modified monovinylidene, aromatic resins, polyetherimides, polyamides, polyester carbonates, polyphenylene sulphides, polyamideimides, polyesteramides, polyether esters, polyetherimide esters, polyarylates, polymethylpentenes, polysulfones, polyethersulfones, polystyrenes, rubber modified high impact polystyrenes, acetyles, styrene maleic anhydride copolymers, acrylonitrile styrene acrylate copolymers, polyphenylene ethers, polyether ketones, chlorinated polymers, fluorinated polymers, and liquid crystal polymers.

3. A polymeric composition according to claim 2, wherein the thermoplastic resins are selected from the group consisting of polyurethanes, polycarbonates and rubber modified monovinylidene aromatic resins and blends thereof.

4. A polymeric composition according to claim 3, wherein the thermoplastic resin is a polyurethane resin.

5. A polymeric composition according to any one of claims 1 to 4, wherein the mica or micaceous material is present in an amount sufficient to absorb laser radiation.

6. A polymeric composition according to claim 5, wherein the amount of mica ranges from 0.05 to 1 percent by weight based on the total weight of the composition.

7. A polymeric composition according to claim 6, wherein the amount of mica present is about 0.3 percent by weight based on the total weight of the composition.

8. A polymeric composition according to any one of claims 1 to 7, wherein the metallic sulphide is selected from the group consisting of copper sulphide; cadmium sulphide, iron sulphide, cobalt sulphide, nickel sulphide and zinc sulphide.

9. A polymeric composition according to claim 8, wherein the metallic sulphide is zinc sulphide.

10. A polymeric composition according to any one of claims 1 to 9, wherein the amount of metallic sulphide in the polymeric composition is sufficient to produce a dark marking on an article moulded from the said polymeric composition when it has been irradiated with a laser beam at a radiation level of 10-20 ampere at a frequency of 1-20kHz in the range of 500-2100nm.

11. A polymeric composition according to claim 10, wherein the amount of metallic sulphide ranges from 0.3 to 3 percent by weight based on the total weight of the composition.

12. A polymeric composition according to claim 11, wherein the metallic sulphide is zinc sulphide and is present in an amount of about 1.7 percent by weight based on the total weight of the composition.

13. An article moulded using a polymeric composition which includes a polymeric material, mica or a micaceous material, and a metallic sulphide; wherein such moulded article is adapted to exhibit dark markings in areas irradiated with a laser beam.

14. An unmarked moulded article according to claim 13, wherein the polymeric material are thermoplastic resins selected from the group consisting of polyolefins, polyurethanes, polycarbonates, polyolefins, polycarbonates,

polyesters, rubber modified monovinylidene, aromatic resins, polyetherimides, polyamides, polyester carbonates, polyphenylene sulphides, polyamideimides, polyesteramides, polyether esters, polyetherimide esters, polyarylates, polymethylpentenes, polysulfones, polyethersulfones, polystyrenes, rubber modified high impact polystyrenes, acetyles, styrene maleic anhydride copolymers, acrylonitrile styrene acrylate copolymers, polyphenylene ethers, polyether ketones, chlorinated polymers, fluorinated polymers, and liquid crystal polymers.

15. An unmarked moulded article according to claim 14, wherein the thermoplastic resins are selected from the group consisting of polyurethanes, polycarbonates and rubber modified monovinylidene aromatic resins and blends thereof.

16. An unmarked moulded article according to claim 15, wherein the thermoplastic resin is a polyurethane resin.

17. An unmarked moulded article according to any one of claims 13 to 16, wherein the mica or micaceous material is present in an amount sufficient to absorb the laser radiation.

18. An unmarked moulded article according to claim 17, wherein the amount of mica material ranges from 0.05 to 1 percent by weight based on the total weight of the composition.

19. An unmarked moulded article according to claim 18, wherein the amount of mica material is about 0.3 percent by weight based on the total weight of the composition.

20. An unmarked moulded article according to any one of claims 13 to 19, wherein the metallic sulphide is selected from the group consisting of copper sulphide; cadmium sulphide, iron sulphide, cobalt sulphide or nickel sulphide.

21. An unmarked moulded article according to claim 20, wherein the metallic sulphide is zinc sulphide.

22. An unmarked moulded article according to any one of claims 13 to 21, wherein the amount of metallic sulphide in the polymeric composition is sufficient to produce a dark marking on an article moulded from the said polymeric composition when it has been irradiated with a laser beam at a radiation level of 10-20 ampere at a frequency of 1-20kHz in the range of 500-2100nm.

23. An unmarked moulded article according to claim 22, wherein the amount of metallic sulphide ranges from 0.3 to 3 percent by weight based on the total weight of the composition.

24. An unmarked moulded article according to claim 23, wherein the metallic sulphide is zinc sulphide and is present in an amount of 1.7 percent by weight based on the total weight of the composition.

25. An unmarked moulded article as claimed in any one of claims 13 to 24 where the moulded article is coloured in any one of the colours pink, red, yellow, orange, lime green, lilac, mid to light blue or turquoise.

26. An unmarked moulded article as claimed in any one of claims 13 to 25 which is a livestock ear tag.

27. A method of producing a moulded article having laser marked surface portions, which method includes:

(a) providing a polymeric material;

(b) compounding said polymeric material with mica or a micaceous material and a metallic sulphide to provide a polymeric composition;

(c) moulding an article using the polymeric composition; and

(d) irradiating said article with a laser beam to produce laser marked surface portions on the article.

28. A method according to claim 27, wherein the polymeric material are thermoplastic resins selected from the group consisting of polyolefins, polyurethanes, polycarbonates, polyolefins, polycarbonates, polyesters, rubber modified monovinylidene, aromatic resins, polyetherimides, polyamides, polyester carbonates, polyphenylene sulphides, polyamideimides, polyesteramides, polyether esters, polyetherimide esters, polyarylates, polymethylpentenes, polysulfones, polyethersulfones, polystyrenes, rubber modified high impact polystyrenes, acetyles, styrene maleic anhydride copolymers, acrylonitrile styrene acrylate copolymers, polyphenylene ethers, polyether ketones, chlorinated polymers, fluorinated polymers, and liquid crystal polymers.

29. A method according to claim 28, wherein the thermoplastic resins are selected from the group consisting of polyurethanes, polycarbonates and rubber modified monovinylidene aromatic resins and blends thereof.

30. A method according to claim 29, wherein the thermoplastic resin is a polyurethane resin.

31. A method according to any one of claims 27 to 30, wherein the mica or micaceous material is present in an amount sufficient to absorb the laser radiation.

32. A method according to claim 31, wherein the amount of mica material ranges from 0.05 to 1 percent by weight based on the total weight of the composition.

33. A method according to claim 32, wherein the amount of mica material is 0.3 percent by weight based on the total weight of the composition.

34. A method according to any one of claims 27 to 33, wherein the metallic sulphide is selected from the group consisting of copper sulphide; cadmium sulphide, iron sulphide, cobalt sulphide or nickel sulphide.

35. A method according to claim 34, wherein the metallic sulphide is zinc sulphide.

36. A method according to any one of claims 27 to 35, wherein the amount of metallic sulphide in the polymeric composition is sufficient to produce a dark marking on an article moulded from the said polymeric composition when it has been irradiated with a laser beam at a radiation level of 10-20 ampere at a frequency of 1-20kHz in the range of 500-2100nm.

37. A method according to claim 36, wherein the amount of metallic sulphide ranges from 0.3 to 3 percent by weight based on the total weight of the composition.

38. A method according to claim 37, wherein the metallic sulphide is zinc sulphide and is present in an amount of about 1.7 percent by weight based on the total weight of the composition.

39. A method as claimed in any one of claims 27 to 38, wherein the article moulded is a livestock ear tag.

40. A method as claimed in any one of claims 27 to 39, wherein the polymeric composition includes one or more pigments such that the article once moulded is coloured pink, red, yellow, orange, lime green, lilac, mid to light blue or turquoise.

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